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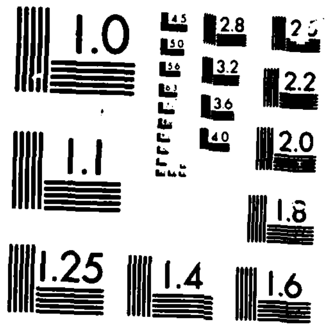

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by

Xi-Yi Huang and Thomas F. George

Prepared for Publication

in

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Vibrational excitation and relaxation of a molecule adsorbed on a surface is investigated. The phase relaxation is seen to assist the laser-driving force in overcoming the anharmonic and/or detuning bottleneck. The incoherent thermalization processes in the initial stage of the admolecular multiphoton excitation are evaluated. It is found that phase relaxation (dephasing) due to the surface and admolecular perturbation plays an important role in the thermalization processes.

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ENERGY AND PHASE RELAXATION IN LASER-INDUCED ADMOLECULAR PROCESSES

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ABSTRACT

Vibrational excitation and relaxation of a molecule adsorbed on a surface is investigated. The phase relaxation is seen to assist the laser-driving force in overcoming the anharmonic and/or detuning bottleneck. The incoherent thermalization processes in the initial stage of the admolecular multiphoton excitation are evaluated. It is found that phase relaxation (dephasing) due to the surface and admolecular perturbation plays an important role in the thermalization processes.

MODEL

The IR-laser-driven resonant active mode absorbs photons and transfers its energy to other vibrational modes or the surface. Statistical thermodynamical behavior may occur in the resulting desorption/dissociation processes. We confine ourselves to the excitation and relaxation of the active anharmonic vibrational mode which is driven by a nearly resonant coherent field and controlled by both energy (T_1) and phase (T_2) relaxation. We treat the many other inactive modes and surface excitation as a large thermal reservoir, by which dissipation mechanisms are provided.

A generalized master equation which considers the anharmonicity and phase and energy dissipation of the active mode has been derived.[1-3] For the case of (1) low bath temperatures, i.e., where the average excitation of the bath quantum $\bar{m}_B$ is much less than unity, and (2) where the rate of phase relaxation η is much larger than the energy relaxation κ and the Rabi frequency Ω_R, the generalized master equation leads to the following coupled differential equations:

$$\dot{W}_m = 2\kappa(\bar{m}_B+1)[(m+1)W_{m+1} - mW_m] + 2\kappa\bar{m}_B[mW_{m-1} - (m+1)W_m]$$

$$+ 2\eta\Omega_R^2(t)\left\{\frac{m(W_m - W_{m-1})}{\eta^2 + [2\varepsilon(m-1)-\Delta]^2} + \frac{(m+1)(W_m - W_{m+1})}{\eta^2 + (2\varepsilon m-\Delta)^2}\right\} \quad . \quad (1)$$

Here W_m is the population of the m-th vibrational level, ε is the anharmonicity, and Δ is the laser detuning. These equations take both the laser coherent excitation and the thermal excitation and relaxation into account.

Phase relaxation (dephasing) is seen to be more important than energy relaxation in the active-mode thermalization process. We have found that when η is large, such as $\eta = 15$ shown in Fig. 1, the population distribution in the active mode is close to a thermal Planck distribution. We have also found that the energy relaxation constant κ has a minor influence on the thermalization of the driven active mode.

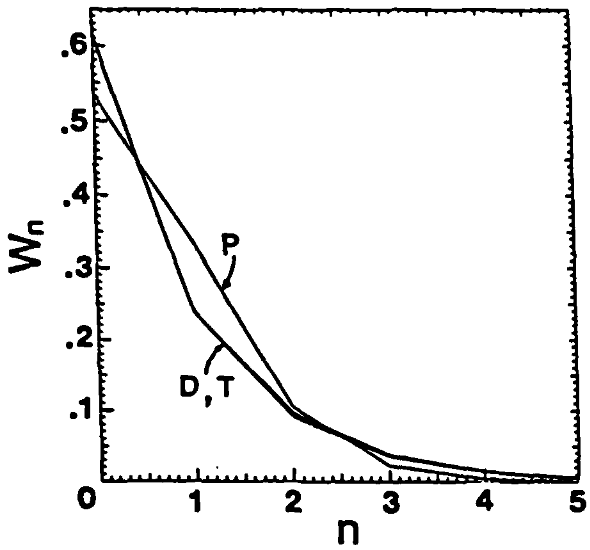

Fig. 1. Level population W_m for : (a) a driven damped anharmonic oscillator (D); (b) Poisson distribution (P); and (c) thermal distribution (T). The same $\bar{m}$ is used for all cases, and $\eta = 15$ is chosen.

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